

Claims

1. A catalyst for use in a Fischer-Tropsch synthesis reaction which comprises cobalt supported on alumina, in which: the catalyst average particle size is in the range 20 to 100  $\mu\text{m}$ ; the specific surface area of the impregnated and calcined catalyst particles is greater than 80  $\text{m}^2/\text{g}$ ; the average pore size of the impregnated and calcined catalyst is at least 90 $\text{\AA}$  (9nm); and the pore volume of the impregnated and calcined catalyst is greater than 0.35  $\text{cm}^3/\text{g}$ .
2. A catalyst as claimed in Claim 1, in which the specific surface area of the catalyst particles is in the range 120 to 220  $\text{m}^2/\text{g}$ .
3. A catalyst as claimed in Claim 1, in which the particle size range is 40 to 80  $\mu\text{m}$ .
4. A catalyst as claimed in any preceding Claim, in which the average pore size of the catalyst is at least 110 $\text{\AA}$  (11nm).
5. A catalyst as claimed in Claim 4, in which the average pore size is at least 130 $\text{\AA}$  (13 nm).
6. A catalyst as claimed in Claim 1 in which the specific surface area of the impregnated and calcined catalyst is less than 120  $\text{m}^2/\text{g}$  and the average pore size is at least 130 $\text{\AA}$  (13nm).
7. A catalyst as claimed in any preceding Claim, in which the pore volume of the catalyst is at least 0.45  $\text{cm}^3/\text{g}$ .
8. A catalyst as claimed in any preceding Claim, incorporating less than

3% by weight of a promoter.

9. A catalyst as claimed in Claim 8, in which the promoter is rhenium or platinum.

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10. A catalyst as claimed in any preceding Claim, in which the support material is  $\gamma$ -alumina .

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11. A catalyst as claimed in Claim 10, in which the  $\gamma$ -alumina is stabilised with a stabilising agent.

12. A catalyst as claimed in Claim 11, in which the  $\gamma$ -alumina is stabilised with lanthanum.

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13. A catalyst as claimed in any preceding Claim, in which the alumina support includes a binder.

14. A catalyst as claimed in Claim 13, in which the binder represents less than 25% by weight of the catalyst.

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15. A catalyst as claimed in Claim 13 or Claim 14, in which the binder is an alumina-containing binder material.

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16. A catalyst as claimed in any preceding Claim, in which the specific surface area of the prepared catalyst, comprising the cobalt in an active catalytic form on the support, is in the range 125 to 160 m<sup>2</sup>/g.

17. A catalyst as claimed in any preceding Claim, in which the cobalt content of the catalyst is from 10 to 40% by weight.

18. A catalyst as claimed in Claim 17, in which the cobalt content is from 15 to 25% by weight.
- 5 19. A process for the production of a catalyst as claimed in any preceding Claim, which comprises: impregnating an alumina support with cobalt and optionally a promoter, optionally drying at less than 120°C, calcining the impregnated support at a temperature in the range 300 to 500°C and treating the calcined catalyst with a reducing gas at an activation temperature in the range  
10 250 to 500°C; the alumina support prior to impregnation having a specific surface area in the range 80 to 225 m<sup>2</sup>/g and a pore diameter in the range 110 to 400Å (11 to 40nm).
- 15 20. A process as claimed in Claim 19, in which the alumina support has a pore volume in the range 0.6 to 1.0 cm<sup>3</sup>/g, prior to impregnation.
21. A process as claimed in Claim 19 or Claim 20, in which the peak calcination temperature is in the range 300 to 450°C.
- 20 22. A process as claimed in any of Claims 19 to 21, in which the activation temperature is in the range 300 to 500°C.
23. A process as claimed in Claim 22, in which the activation temperature is in the range 300 to 450°C.  
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24. A process as claimed in any of Claims 19 to 23, in which the calcination is carried out for between 0.5 and 6 hours.
25. A process as claimed in any of Claims 19 to 24, in which the activation

treatment is carried out for between 1 and 10 hours.

26. A process as claimed in any of Claims 19 to 25 in which the reducing gas is hydrogen and/or carbon monoxide, optionally mixed with an inert gas.

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27. A process as claimed in any of Claims 19 to 26, in which, prior to impregnation, the support is pre-calcined at a temperature in the range of 400 to 900°C.

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28. A process as claimed in any of Claims 19 to 27, in which the alumina support is  $\gamma$ -alumina and the process includes the step of stabilising the  $\gamma$ -alumina prior to the calcination step.

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29. A process as claimed in any of Claims 19 to 28, in which prior to impregnation, the alumina support has a specific surface in the range 150 to 240 m<sup>2</sup>/g.

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30. A process as claimed in any of Claims 19 to 29, in which, prior to impregnation, the alumina support has a pore volume in the range 0.7 to 0.9 cm<sup>3</sup>/g.

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31. A process as claimed in any of Claims 19 to 30, in which the impregnation step comprises an incipient wetness treatment in which an aqueous solution of a cobalt compound and optionally a rhenium compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the calcining step.

32. A process as claimed in Claim 31, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore

volume of the catalyst support.

33. A process as claimed in Claim 31 or Claim 32, in which drying is carried out at 80 to 120°C.

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34. A process as claimed in any of Claims 31 to 33, in which the cobalt compound is selected from cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ), cobalt acetate(s), cobalt halide(s), cobalt carbonyl(s), cobalt oxalate(s), cobalt phosphate(s), cobalt carbonate(s), cobalt (hexa)amine salt(s) and organic cobalt compounds.

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35. A process as claimed in any of Claims 31 to 34, in which the rhenium compound is selected from perrhenic acid ( $\text{HReO}_4$ ), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).

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36. A process as claimed in Claim 35, in which the cobalt compound is cobalt nitrate and the rhenium compound is perrhenic acid.

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37. A process as claimed in any of Claims 19 to 25, in which, prior to impregnation, the alumina support has an ASTM attrition value of less than 30% by weight of fines produced by 5 hours testing.

38. A process as claimed in Claim 37 in which the ASTM value is less than 20%.

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39. The use of a catalyst as claimed in any of Claims 1 to 18 in a Fischer-Tropsch synthesis reaction.

40. The use of a catalyst manufactured according to a process as claimed in any of Claims 19 to 38 in a Fischer-Tropsch synthesis reaction.

41. The use of a catalyst as claimed in Claim 39 or Claim 40, in which the reaction is carried out in a slurry bubble column reactor.

5 42. A use as claimed in Claim 41, in which H<sub>2</sub> and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H<sub>2</sub> and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

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43. A process for the production of hydrocarbons which comprise subjecting H<sub>2</sub> and CO gases to a Fischer-Tropsch synthesis reaction in a reactor in the presence of a catalyst as claimed in any of Claims 1 to 18.

15 44. A process for the production of hydrocarbons which comprise subjecting H<sub>2</sub> and CO gases to a Fischer-Tropsch synthesis reaction in the presence of a catalyst manufactured according to a process as claimed in any of Claims 19 to 38.

20 45. A process as claimed in Claim 43 or Claim 44, in which the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid.

25 46. A process as claimed in Claim 45, in which the reaction is carried out in a slurry bubble column reactor.

47. A process as claimed in Claim 46, in which the H<sub>2</sub> and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H<sub>2</sub> and CO, the catalyst being

maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

5 48. A process as claimed in any of Claims 43 to 47, in which the reaction temperature is in the range 190-250°C.

49. A process as claimed in Claim 48, in which the reaction temperature is in the range 200-230°C.

10 50. A process as claimed in any of Claims 43 to 49, in which the reaction pressure is in the range 10-60 bar.

15 51. A process as claimed in Claim 50, in which the reaction pressure is in the range 15 to 30 bar.

52. A process as claimed in any of Claims 43 to 51, in which the H<sub>2</sub>/CO ratio of the gases supplied to the Fischer-Tropsh synthesis reactor is in the range 1.1 to 2.2.

20 53. A process as claimed in Claim 52, in which the H<sub>2</sub>/CO ratio is in the range 1.5 to 1.95.

25 54. A process as claimed in any of Claims 43 to 53, in which the superficial gas velocity in the reactor is in the range 5 to 60 cm/s.

55. A process as claimed in Claim 54 in which the superficial gas velocity is in the range 20 to 40 cm/s.

56. A process as claimed in any of Claims 43 to 55, in which the product of

the Fischer-Tropsch synthesis reaction is subsequently subjected to post-processing.

57. A process as claimed in Claim 56 in which the post-processing is  
5 selected from de-waxing, hydro-isomerisation, hydro-cracking and combinations of these.

58. A catalyst support in which the catalyst average particle size is in the  
range 20 to 100  $\mu\text{m}$  and the average pore size of the catalyst is at least 90Å  
10 (9nm).

59. A catalyst support as claimed in Claim 58, having a pore volume greater than 0.6  $\text{cm}^3/\text{g}$ .

60. Catalyst support as claimed in Claim 58 or Claim 59, having a specific  
15 surface area greater than 100  $\text{m}^2/\text{g}$ .

61. Catalyst support as claimed in any of Claims 58 to 60, in which the  
support material is silica, titanium dioxide or alumina.  
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62. Catalyst support as claimed in Claim 58, in which the support material is  
alumina.

63. Catalyst support as claimed in any of Claims 58 to 62 having an ASTM  
25 attrition value of less than 20.